Investigation of leakages in PEFC by measuring current density distribution and Raman spectra

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Introduction

Reliability is an important factor for the commercialization of fuel cells. Gradual degradation of electrodes and gas diffusion media does not affect severely the reliability as the operation conditions can be adapted to the state of health of the cell. However, complete breakdown of fuel cell systems due to membrane fissure is a severe problem which has to be identified as soon as possible. The formation of leakages in the membrane or sealings in PEFC is a relatively frequent malfunction which leads to loss of fuel cell functionality. Leakage in the membrane may occur due to defects introduced in the membrane or the membrane-electrode-assembly manufacturing process (e.g., penetration of the membrane by a carbon GDL fiber), an incorrect assembling of the fuel cell and fast dry-wet cycling of the membrane. A cross-over of gases result in heat evolution and further damage to the membrane and sealing. Therefore, an early detection of leakages is important for safety as well as for reliability of cell operation. Here we report the combined analysis of a membrane hole by current density and non-resonant Raman spectroscopy. Raman scattering is induced by laser irradiation in the flow channels and back-scattered light detection by a monochromator/ CCD-camera.

Experimental

A single cell with a segmented printed circuit board (PCB) at the anode is operated with hydrogen as fuel and air as oxidant. The PCB technology from DLR has been described in detail elsewhere [1, 2]. Images of the PCB board is despicted in Fig. 1 and the principle of function in Fig. 2 and Fig. 3. The resistor array for the current measurement is integrated in the PCB using a multi-layer assembly. The flow field channels can be machined directly into the plate. The current collector segments of the measuring board are gold plated to decrease the contact resistance and to avoid corrosion. The sense wire connectors on the segmented bipolar plate are connected to a data acquisition unit consisting of a multiplexer and a digital multimeter (Fig. 4).

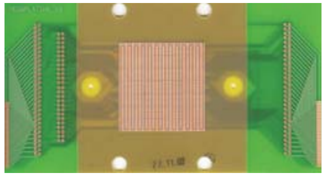


Fig. 1: Example of segmented bipolar plate with 49 segments for single cell and stack use (single channel sepentine flow field channels integrated)

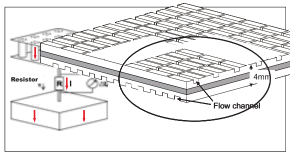


Fig. 2: Scheme of the segmented bipolar plates for current density measurements

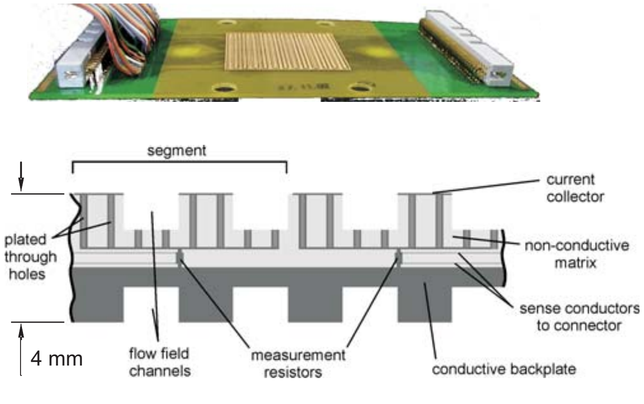


Fig. 3: Photography of a segmented bipolar plate and scheme of the printed circuit technology for current density measurements

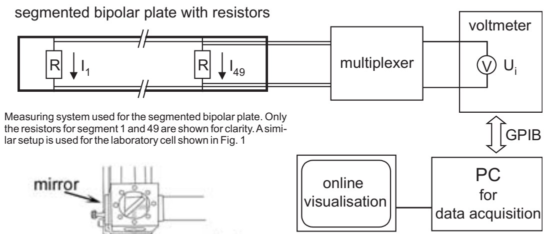
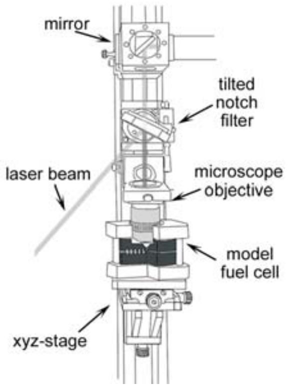


Fig. 4: Measuring system used for the segmented bipolar plate. Only the resistors for segment 1 and 49 are shown for clarity. A similar setup is used for the laboratory cell shown in Fig. 1



The experimental setup for recording Raman gas signals was realized by a specifically designed single cell. A hole (1mm) is introduced to access the anodic flow field. The flow field was sealed by a thin sapphire glass window. An objective (10x, working distance: 15 mm, NA: 0.25) focusses the light of a laser (e.g., Ar+, 488 nm, 3.2 W power, exposure time 3 min) into the flow field channel and collects the scattered light. The scattered light was directed to the spectrograph (HoloSpec f/1.8i, Kaiser Optical Systems) / CCD-camera unit via a notch filter which rejects Rayleigh scattering (Fig. 5). The measurements were carried out using a commercially available sulphonated PTFE membrane with 0.4 $mgcm^{-2}$ Pt loading on both electrodes. Room temperature operation without external humidification is used.

Fig. 5: Central part of the Raman microscope setup

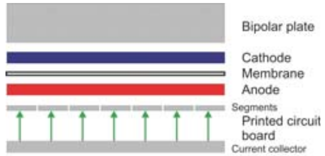


Fig. 6: Scheme of current density measurement configuration with the printed circuit board under normal conditions

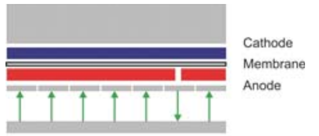


Fig. 7: Scheme of current density measurement under open circuit conditions with a leakage in the membrane

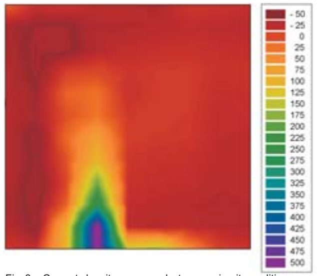


Fig. 8: Current density measured at open circuit conditions on a MEA with a leakage

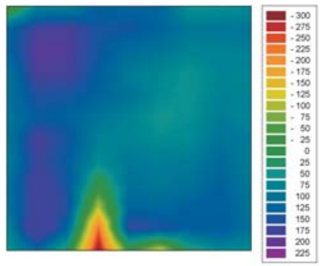


Fig. 9: Current density measured under load (approx. 100 mA/cm2) on a MEA with a leakage

Results

The current density measurements of a "normally operated" cell are related to the local reaction rates. Normal operation here refers to the absence of leakages, flooding, and/or fuel starvation. Under open circuit conditions the total (integral) current is zero independently of the operating conditions. However, even at open circuit conditions some variations over the active area occur. One observes different current directions in some areas, so that in the "normally operated" fuel cell, fluctuations in the local current density with a few $mAcm^{-2}$ are typical.

Applying a load to the cell leads to increased current densities in the segments as well as larger variations between segments. These are related to local variations in the operating conditions, whereas the local humidification is of major importance [3]. In all segments the current is directed in the same direction (Fig. 6).

With a leakage the variations of the local operating conditions are dramatic. In particular the composition of the reactants is changed in the case of leakages since both hydrogen and oxygen are mixed and react. Consequently, a local mixed potential is formed at the leakage. In this case, hydrogen cross-over is larger due to higher diffusion and concentration than oxygen cross-over, especially if the cell is operated with air. Consequently, the changes of the local potential are more significant at the cathode compared to the anode.

Fig. 8 shows the current density measured for a cell with a leakage under open circuit conditions. The current density distribution shows a distinct current density distribution that clearly indicates the presence of the leakage. In the area next to the leakage, a positive current direction is observed which corresponds to the expected behavior. In contrast to that, in most of the residual areas the current direction corresponds to an electrolysis mode (Fig. 8). Open circuit conditions dictate an overall cancellation of the current density. This means that a local electrochemical reaction induces an inverse electrochemical reaction in the surroundings (at another place) which is evident in Fig. 9.

When applying a load to the cell, the local operating conditions change completely and the current density measurement on the cell with a leakage is shown in Fig. 8. In this case the areas operating in the "fuel cell" mode and in the "electrolysis" mode are inversed compared to the open circuit conditions (Fig. 8). The leakage area can clearly be detected by high negative current densities indicating the electrolysis mode.

The Raman spectra detect the passage of N_2 from the cathode to the anode (Fig. 10) through the hole. The amount of N_2 depends on the pressure of H_2. O_2 could only be detected at high air flows. Interestingly, hydrogen could not be detected in the cathode air flow for usual cell operation. However, when the air flow is decreased below the flow of hydrogen, Raman signals of H_2 are present. Liquid water resulting either from the electrochemical or chemical reaction is also detected next to the hole. Water generation by the chemical reaction is supported by a strong increase of temperature around the hole. The temperature increase was observed by measuring the intensity changes of rotational Raman bands of H_2 that simply follow a Boltzmann distribution. This relation estimated the local temperature around the hole to about 98°C while the global temperature of the fuel cell remained near room temperature.

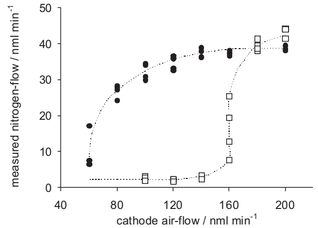


Fig. 11: Flow of nitrogen detected at the anode side as a function of cathode air flow in the case of a damaged membrane at two different cell powers; dark circles: 500 mA; white squares: 1000 mA

Conclusions

Current density measurements allow to identify leakages in cells. Especially under open circuit conditions areas operating in "electrolysis mode" as well as areas operating in the "fuel cell mode" coexist under stationary conditions. At applied load the current density distribution also reflects the existence of the leakage whereas the effect is complex and depends on operation conditions. Although at present the current density distributions of cells with leakages are not modelled, it is clear that current density measurements are a suitable tool for leakage detection. Future investigations using the PCB method for current density measurement on both electrodes will be performed in order to clarify the effect. In particular it is necessary to ascertain that the current density on anode and cathode are symmetrical and to estimate the influence of the GDL. Alternatively, Raman spectroscopy seems to be a promising tool to monitor composition changes of reaction gases and thereby contributes to understanding of cell behaviour.

Acknowledgement

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References

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